

# Fabrication of High Strength Metal-Carbon Nanotube Composites

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## ABSTRACT

A major objective of Army technology is the development of lighter and stronger platforms such as armored vehicles for Future Combat systems and Future Force. Here we show that carbon nanotubes could be the basis of such a possibility. It is shown for the first time that a carbon nanotube-iron composite, iron being the principle component of steel, has significantly enhanced mechanical strength. The major challenge has been to develop methods to incorporate single walled carbon nanotubes (SWNTs) into metals. Here we report the first successful fabrication of a metal-SWNT composite having significantly enhanced yield strength. A direct and controllable method of incorporating SWNTS into iron, the principal component of steel, has been developed.

## 1 INTRODUCTION

Single Walled Carbon Nanotubes (SWNTS) illustrated in figure 1 are tubes made of carbon having graphite-like structure. They can be envisioned as sheets of graphite

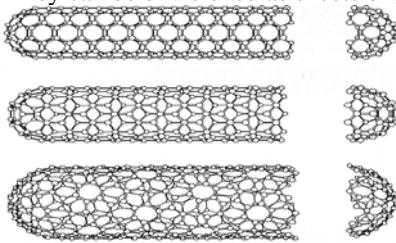


Figure 1: Carbon nanotubes with single walls showing the three different chiral structures

rolled into tubes. Typically they are hundreds of microns long and have diameters of 0.05 to 0.2 microns making them the thinnest known fibers. They have tensile strengths 20 times that of steel. Since carbon nanotubes have the highest tensile strength of any known fiber and the largest aspect ratio, they should be the ultimate reinforcing fiber. Up until now there have been no reports of significant enhancements of yield strength in carbon nanotube metal composites. The major challenge has been to develop methods to incorporate SWNTS into metals. Here we report the first successful fabrication of a metal-SWNT composite having significantly enhanced yield strength. Carbon nanotubes SWNTs have been extensively investigated for

developing polymer matrix nanocomposites and a number of such nanocomposites are already being used in various applications [Morgan, 2007]. Until this work there have been no successful fabrication of metal-SWNT composites having significantly enhanced mechanical strength.(Rohatgi and Schultz, 2007) In one study, 5% to 10 % by weight of pre-synthesized arc-grown multiwall carbon nanotubes were dispersed in aluminum matrices resulting in an increase of hardness, but no tensile strength measurements were performed. (Zhong, et al, 2002) In another study mechanical dampening characteristics of MWNT (multi walled carbon nanotubes)/magnesium composites formed by high pressure infiltration were studied and compared with that for the pristine metal matrix, but no significant improvement was observed. (Yang and Schaller, 2004) A detailed study was performed by (Flahaut, et al, 2000) using pre-synthesized nanotubes, which were then hot pressed with iron and  $\text{Al}_2\text{O}_3$ . The nanotubes suffered significant damage due to the high temperatures of around 1500-1600 °C used in this process and no substantial increase in mechanical properties was reported. (Goh, et al, .2006) studied reinforced magnesium matrices with carbon nanotubes using powder metallurgy techniques and reported an increase of only 0.2% in yield strength and 0.18 % in ductility. Some of the issues which preclude mechanical property enhancement in metal-nanotube composites arise due to the high processing temperatures used in infiltrating pre-synthesized nanotubes into the metal matrix. Moreover, the methods used do not lead to good dispersion of the nanotubes in the metal matrix and efficient nanotube-metal contact and pinning. We have developed a scaleable chemical vapor infiltration technique which forms metal matrix nanocomposites with enhanced yield strength.[Goyal, et al, 2006, 2007] Specifically, catalytic chemical vapor deposition was used to infiltrate metal matrices with single and multiwall carbon nanotubes using carbon monoxide and acetylene as carbon sources. Vickers hardness numbers and stress-strain curves were measured to characterize the mechanical properties of the composites formed.

## 2 EXPERIMENTAL

The catalyst and promoter precursors, iron acetate, cobalt acetate and molybdenum acetate, each 0.01 weight % of total solution, respectively, were dissolved in ethanol.

Report Documentation Page			Form Approved OMB No. 0704-0188		
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1. REPORT DATE <b>DEC 2008</b>	2. REPORT TYPE <b>N/A</b>	3. DATES COVERED <b>-</b>			
<b>4. TITLE AND SUBTITLE</b> <b>Fabrication of High Strength Metal-Carbon Nanotube Composites</b>			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
<b>6. AUTHOR(S)</b>			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> <b>US Army Research, Development and Engineering Center, Picatinny, New Jersey 07806</b>			<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>		
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>			<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>		
			<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>		
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> <b>Approved for public release, distribution unlimited</b>					
<b>13. SUPPLEMENTARY NOTES</b> <b>See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.</b>					
<b>14. ABSTRACT</b>					
<b>15. SUBJECT TERMS</b>					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  <b>UU</b>	<b>18. NUMBER OF PAGES</b>  <b>5</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>
<b>a. REPORT</b> <b>unclassified</b>	<b>b. ABSTRACT</b> <b>unclassified</b>	<b>c. THIS PAGE</b> <b>unclassified</b>			

Typically 3-5 gms of micron-sized iron powder was soaked in this solution, dried, and pressed into thin cylindrical pellets under an applied load of 5000 Kg. The pellets were 13 mm in diameter and between 4 and 5 mm in thickness with densities of 5.7 to 6.10 gm/cc. The average porosities of all the samples used in the mechanical measurements were the same. The catalyst loading in our samples was very low. The amount of catalyst metal in the iron matrix was estimated to be about 0.003 weight % of the total weight of the pellet.

The pellets were placed in a quartz boat in a horizontal quartz tube high temperature furnace. The quartz tube was pumped down to about  $10^{-3}$  torr. In case of SWNTs, the reactor was back-filled with flowing pure hydrogen for 30 minutes to an hour to reduce the oxides to metals at 500°C. In the second step the carbon source, carbon monoxide (CO), was introduced at 700°C into the reactor at a flow rate of 100 standard cubic centimeters per minute (sccm) for 30 to 60 minutes- to deposit SWNTs within the matrix. In the case of MWNTs a single step protocol involving heating to 800°C under flowing argon followed by switching the gas flow to a mixed carbon source of acetylene, CO and argon with flow rates of 6, 100 and 300 sccm, respectively, at atmospheric pressure, was used. Reference pellets were prepared with the same weight of iron powder and applied load, followed by the same thermal cycles used to grow SWNTs and MWNTs but without a carbon source. After completion of the deposition, the system was allowed to cool to room temperature under flowing argon.

The characterization of the composites was carried out by micro-Raman spectroscopy, x-ray diffraction (XRD), and field-emission scanning electron microscopy (FE-SEM). Vickers hardness measurements were conducted using a LECO micro-hardness tester (LM 700, LECO Corp.). A load of 10 Kgf (kilogram force) at ambient temperature with a dwell time of 5 seconds was selected, and average values are reported. Stress-strain data were obtained in compression with a MTS servo hydraulic system operated at a constant displacement rate so as to give a strain rate of about 0.00004/sec.

### 3 RESULTS AND DISCUSSIONS

The representative micro-Raman spectra obtained using 632.8 nm laser excitation from the surface of the nanocomposites are shown in Figs. 2a-c. In Fig 2a clear evidence for the formation of SWNTs is provided by the appearance of the characteristic SWNT lines associated with the carbon-carbon bond tangential modes near frequencies of  $1591\text{ cm}^{-1}$  and  $1552\text{ cm}^{-1}$  (the latter appearing as a well-defined shoulder in the spectrum), and the lines at 190, 247, 259 and  $279\text{ cm}^{-1}$  due to the radial breathing modes (RBMs) of individual tubes of different diameters. The line observed at  $293\text{ cm}^{-1}$  is likely to be associated with  $\text{Fe}_2\text{O}_3$  present as an impurity in the iron matrix. The diameters ( $d$ , nm) of the individual SWNTs can

be determined from the RBM frequency  $\omega$ . For bundled SWNTs:  $d = (238/\omega)^{1.075}$  (Alvarez, et al; 2001). The broad line at  $1327\text{ cm}^{-1}$  assigned to defects and amorphous carbon was found to be relatively weak. This indicated that rather defect-free SWNTs are formed with relatively little amorphous carbon present. In Figure 2 b-c the Raman spectrum does not show the relatively sharp radial breathing mode (RBM) lines that are indicative of SWNTs. The lines at about  $1323\text{ cm}^{-1}$  and  $1581\text{ cm}^{-1}$  observed for samples prepared with acetylene mixed with carbon monoxide can be assigned to the disordered (D) and graphitic (G) modes of MWNTs (Thomsen et al, 1999) Concomitant growth of iron carbide also occurs when acetylene alone is used as the carbon feed – this aspect is covered in more detail later in the discussion of the XRD results.

In Figures 3 a-b the diameters of 10 to 20 nm estimated from the FE-SEM images are an order of magnitude larger than the individual SWNT diameters obtained from the RBM Raman frequencies, indicating that the SWNTs formed are bundled into “ropes”. The individual iron particles are likely to be anchored in place by the nanotube bridges. It is estimated from the measured increase in weight after nanotube deposition that typically 1 weight % or 2.2 volume % of SWNTs are incorporated into the

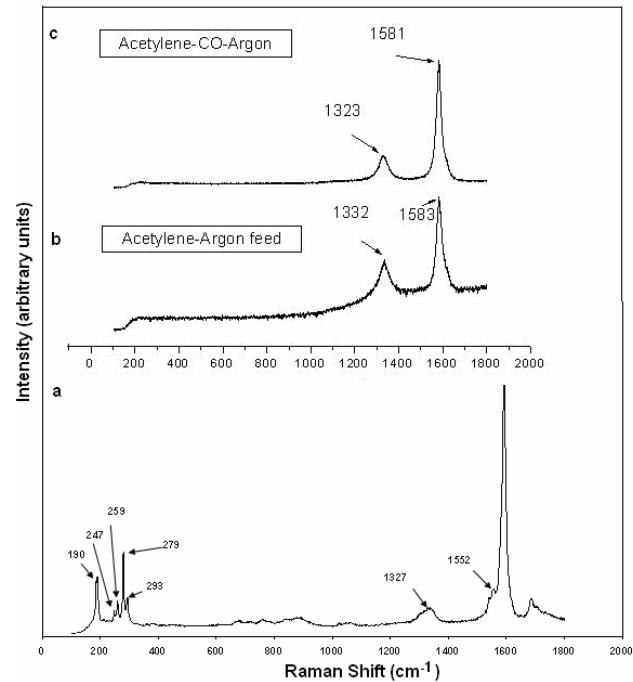


Figure 2: Raman spectra excited at 632.8 nm for: a) iron-SWNT, b) Iron-MWNT with acetylene feed, c) iron-MWNT with CO-acetylene feed.

starting iron matrix. FE-SEM images are consistent with largely MWNT formation, and the images shown in Fig. 3 c and d indicate somewhat denser growth of MWNTs compared to that of SWNTs. Fig. 3c depicts a low

magnification image showing sizable MWNT penetration to a depth of 150 to 160  $\mu\text{m}$ . A lower concentration of nanotubes is evident below 160  $\mu\text{m}$  and through the approximately 0.5 mm thickness of the sample. A high magnification image taken from a region about 160  $\mu\text{m}$  inside the top surface of the composite showing dense growth of MWNTs is displayed in Fig. 3d. Measured weight changes indicate a MWNT loading of up to 1 weight %  $\sim$  4.48 volume % in the optimized iron-MWNT composites, which is similar to that obtained for the iron-SWNT composites.

XRD measurements (Fig. 4a) showed the presence of pure iron as indicated by reflections at  $2\theta$  values of 45, 65, 83, and 99 degrees. XRD reflections from SWNTs are not detected due to the relatively low weight % loading of SWNTs in the nanocomposites. Reflections associated with the iron-rich cementite  $\text{Fe}_3\text{C}$  phase were clearly absent. An XRD line at a  $2\theta$  value of 26 degrees was observed near the expected (001) reflection of graphite, but its intensity is too high for it to be attributed to a carbon phase. We tentatively assign this reflection to an iron sub-oxide formed in the iron matrix under our fabrication conditions. XRD patterns for the composites obtained using acetylene and argon, and a mixture of acetylene, CO and argon, respectively, are shown in Fig. 4b and c. The XRD pattern for the composite prepared using acetylene and argon shows sharp reflections due to iron carbide,  $\text{Fe}_3\text{C}$ , while a mixture of CO, acetylene and argon is carbide free.

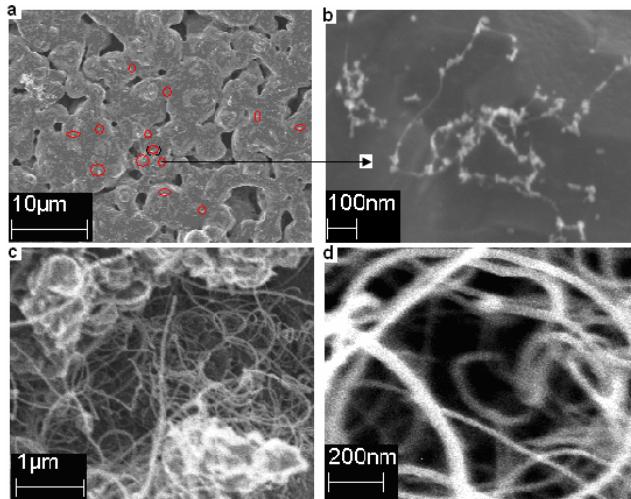
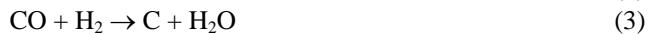


Figure 3: SEM images a) low magnification iron-SWNT, b) higher resolution SWNTs, c-d) MWNTs dispersed in iron matrix.

In order to understand why iron carbides are not formed when acetylene is mixed with CO, we propose the following sequence of reactions during *in-situ* growth with acetylene. The  $\text{Fe}_3\text{C}$  impurity phase is formed by reaction 1 below:



It involves the reduction of  $\text{Fe}_2\text{O}_3$  which is typically present in the iron matrix as an impurity phase, by hydrogen (formed by the initial dissociation of acetylene) followed by the adsorption of carbon from acetylene decomposition. The dissociation of acetylene is further enhanced by the presence of iron as catalyst. Iron is supersaturated with carbon and leads to the formation of iron carbide. Introducing CO initiates the occurrence of concurrent reactions 2 and 3 below. The presence of CO results in the formation of carbon nanotubes and  $\text{CO}_2$  following the disproportionation reaction 2 in the presence of catalysts and reaction 3. In addition to that, reaction 3 scavenges hydrogen to form carbon nanotubes and prevents the reduction of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{C}$  via reaction 1.



The above reaction sequence is consistent with the XRD data, which shows no evidence for the formation of the  $\text{Fe}_3\text{C}$  phase when CO is introduced into the carbon precursor feed.

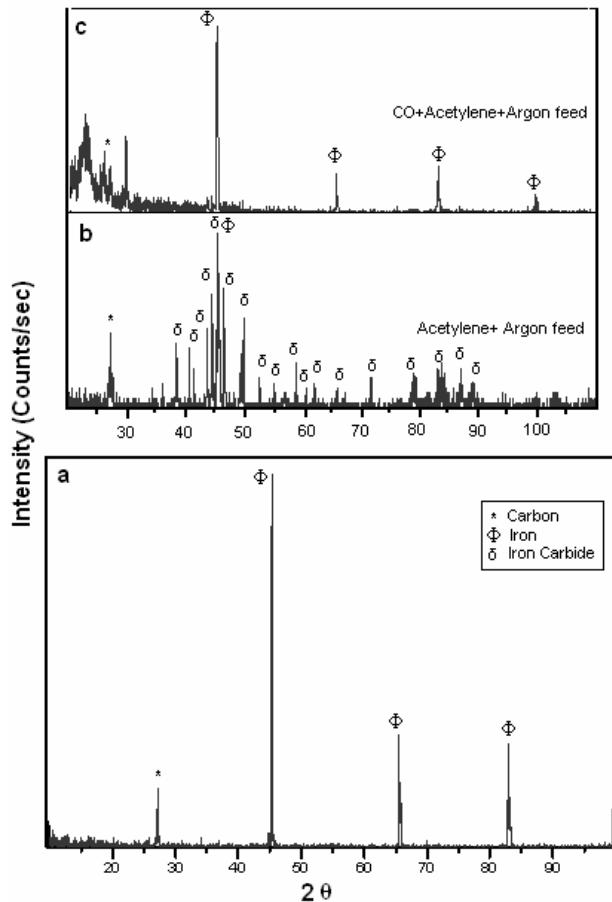


Figure 4: XRD a) iron-SWNT pellet, b) iron-MWNT pellet with acetylene feed, c) iron-MWNT with CO-acetylene.

Compressive stress-strain curves from two representative samples, with and without nanotubes show significant differences. The flow stress, the stress for significant plastic flow, is taken at the intersection of a straight line passing through the initial linear part of the stress-strain curve at low strains and a straight line passing through the linear work hardening part of the curve at larger strains. For the data in Fig. 5a, the flow stress is about 45% higher for the sample containing the SWNTs compared to the value for the reference iron sample. This flow stress is numerically equivalent to a yield stress obtained by a 0.4% strain offset technique. In addition, the work hardening coefficient, the slope in the latter linear part of the stress-strain curve at larger strains, is greater by a factor of about 3.4 (a 240% increase) for the sample containing the SWNTs relative to the reference sample. Thus, the mechanical strength of the sample containing SWNTs is significantly increased and much greater work is required to deform this sample plastically in the work hardening range. Since mechanical properties depend on porosity, it is important to emphasize that the porosity of the reference sample and the sample with SWNTs is the same and therefore differences in porosity cannot account for the enhanced mechanical strength. A sample was ground so as to remove 170  $\mu\text{m}$  from each side and compression tests were repeated. A stress-strain curve taken after grinding again indicates that the flow stress increased by an amount consistent with the work hardening during the initial compressions. Thus, the removal of the thin surface layers containing the highest densities of SWNTs had a minimal effect on the flow stress. These results indicate that the higher flow stresses observed in the samples containing the SWNTs are due to bulk effects and further that the SWNTs are distributed throughout the samples of thicknesses of the order of 0.6 cm. In case of MWNTs, the increase in upper and lower yield strength is 36 and 43% respectively as shown in Fig. 5 b. The lower yield point for the reference sample is at 179 MPa and for the iron-MWNT sample it is at 253.3 MPa. The upper yield point for the reference sample is at 200 MPa and at 276 MPa for the iron-MWNT composite.

The observed increase in strength of the nanotube-iron composites can be attributed to the mechanical support provided within the cavities by the nanotubes. The SWNTs are largely concentrated in cavities in the matrix as indicated by the FE-SEM images shown in Fig. 3. It is well-known that iron is an excellent catalyst towards nanotube growth (Cassell, et al, 19991) and can partially dissolve and bond to carbon to provide supporting bridges at the cavities. Bonding might also occur at nano-sized catalysts embedded in the larger iron particles of the matrix. Because of this support additional dislocation pinning may not be necessary. High porosity decreases mechanical strength because the average stress inside the material is greater than the average applied stress (Wang, 1984, Knudsen, 1959). Providing support in the pores will lower the average stress

in the material, which determines dislocation motion and yield. Thus yield will occur at higher values of the applied stress.

Overall this support at the cavities will offset in part the effect of the cavities in weakening the iron matrix, resulting in higher mechanical strength. The very large increase in the work hardening coefficient or slope suggests that the mechanism of work hardening may be different in the samples containing SWNTs than in the reference samples. For example, if the work hardening of the reference sample of Fig. 5 is due to long range dislocation-dislocation interactions, then the much higher work hardening slope of the sample containing SWNTs may be due to dislocation pile up at barriers introduced by the treatment which this sample received. When these barriers are SWNTs, it is expected that they are located not only in the cavities, but also distributed throughout the iron matrix.

Vickers hardness indices correlate with the tensile strength and fatigue resistance. Typical average values of the Vickers hardness (HV) indices HV/10 (with 10 Kgf) of 95.2 for the reference sample and 135.7 for iron-SWNT sample showed an increase in the hardness index by 74%. For the carbide free iron-MWNT composites Vickers numbers showed enhancement in average hardness by 97.5%, which is substantially higher than that of an iron-SWNT composite with a similar concentration of nanotubes.

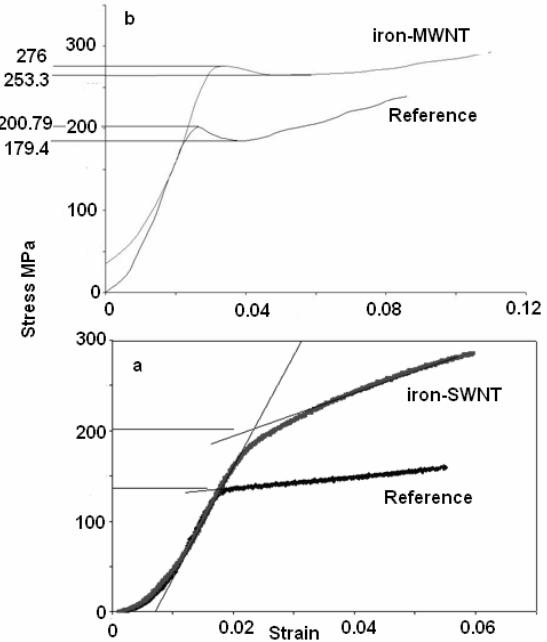


Figure 5: Compressive stress-strain curves for a) iron-SWNT and b) iron-MWNT composite.

#### 4. CONCLUSION

We have developed a scalable chemical vapor infiltration technique which forms metal matrix nanocomposites of single walled and multiwalled carbon nanotubes. Specifically, catalytic chemical vapor deposition was used to infiltrate metal matrices with single and multiwall carbon nanotubes using carbon monoxide and acetylene as carbon sources. Extensive characterization using Raman spectroscopy, XRD and SEM indicate the tubes are bonded to the walls of pores in the material. Stress strain and hardness measurements indicate the composite with 1% by weight of SWNTs has had a 45% increase in yield strength compared with a similarly treated sample without SWNTs.. The work represents the first demonstration of a significant enhancement of the strength of a metal–carbon nanotube composite. The fabrication process should easily be scaled up to produce large quantities of materials and could lead to lighter stronger vehicle and aircraft structures reducing fuel consumption and increasing warfighter survivability.

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